Size effects on melting and wetting in the Ga–Pb nano-alloy

Marco Allione, Richard Kofman, Franck Celestini, Y. Lereah

Size effects on Melting and Wetting in the Ga-Pb Nano-Alloy

Marco Allione[1*] , Richard Kofman[1], Franck Celestini[1] and Yossi Lereah[2,3]

[1] *Laboratoire de Physique de la Matière Condensée, Université de Nice Sophia Antipolis et UMR CNRS N° 6622, Parc Valrose, 06108 Nice Cedex 2, France*

[2] *Wolfson Applied Materials Research Center, Tel-Aviv University, 69978 Tel-Aviv, Israel*

[3]*Department of Physical Electronics, Faculty of Engineering, Tel-Aviv University, 69978 Tel-Aviv, Israel*

Abstract:

Ga-Pb alloys with 15 at% Pb mean concentration have been prepared at the nanoscale by means of evaporation-condensation technique in ultra high vacuum conditions. Transmission electron microscope images indicate that at room temperature, the system is a two-components breath figure composed of liquid Ga nanodrops containing Pb nanocrystals. Some thermodynamic properties of this nano-alloy are investigated for different temperatures and particle sizes. The results obtained put in evidence a large modification of the Ga-Pb bulk phase diagram : a decrease of the melting points of the two components as well as the ones of the miscibility gap. Changes in the microscopic structure of the system as a function of temperature have been investigated and a full wetting transition from a dry to a completly wet state has been put in evidence.

1.Introduction

Metal nanoparticle composites are a very attracting subject of study since many years. Thermodynamics of nanostructured systems are studied since the very beginning, with the first results dating back to the nineteenth century [1]. It is now a well established result now that melting and solidification temperatures of metals are strongly modified in nanocomposites. In particular, it turns out that melting temperature is lowered with respect to the bulk one [2]. So far this property has been investigated in a large number of pure metals in different conditions of size and embedding matrices, but very little is known about metal alloys at nanoscale.

Metal alloys are extremely useful for the variability of their thermodynamical, mechanical and electrical properties that make them suitable for a very wide range of applications. The Ga-Pb alloy system in particular is interesting for the structure of its phase diagram [3] as shown in Fig.1. Ga and Pb being quasi-immiscible at ambient temperature, the diagram shows the existence, between the bulk melting temperatures of the two metals, of two distinct phases, one represented by almost pure liquid Ga, and the other by almost pure solid Pb. Above the melting temperature (327°C) the two liquids coexist for a wide range of temperature to finally mix at about 600°C.

In a recent paper [4], we have investigated the fabrication of Ga-Pb two-components breath figures. We showed that, by condensing Ga and Pb atomic vapours on a substrate, the system self-organises in a breath figure of Ga nanodrops containing each one a Pb nanocrystal.

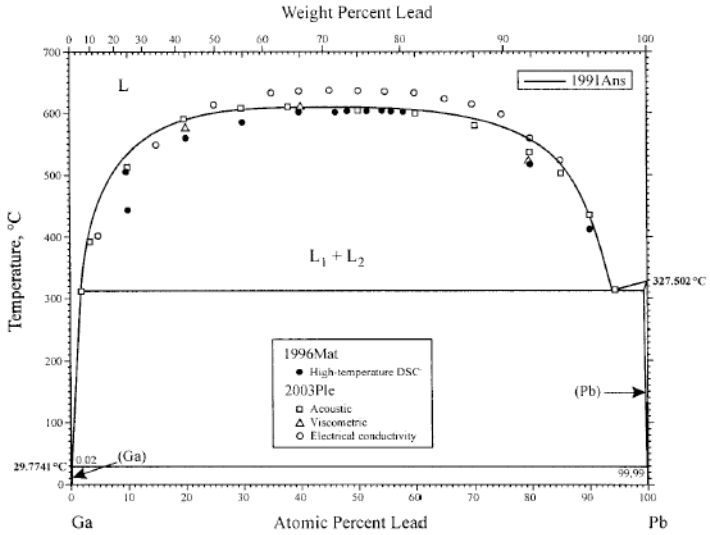

Figure 1. Ga-Pb bulk phase diagram.

In the same paper, we have obtained the Pb concentration in the Ga droplets and shown that it was dependent of size and different from the mean Pb concentration as deposited on the substrate.
In the present work, thermodynamic and structural properties of the Ga-Pb nano-system are investigated versus temperature with an aim of evaluating size effects on the Ga-Pb phase diagram. We finally examine the wetting of Pb in a Ga nanodrop and put in evidence a transition from a completely dry to a completely wet state.

2. Experiments

Production of the Ga-Pb breath figures has already been described [4]. The preparation technique allows the production of alloy nanoparticles of different concentration with average size ranging from few to few hundreds of nanometers. The samples obtained are studied by means of "in situ" electron microscopy with a field-effect cathode Tecnai F20 supplied with CCD and video cameras. Gatan heating and cooling holders were used for adjusting the temperature of the samples between -160°C and 600°C.
The microscope can be operated in different modes giving complementary informations as illustrated in Fig. 2.

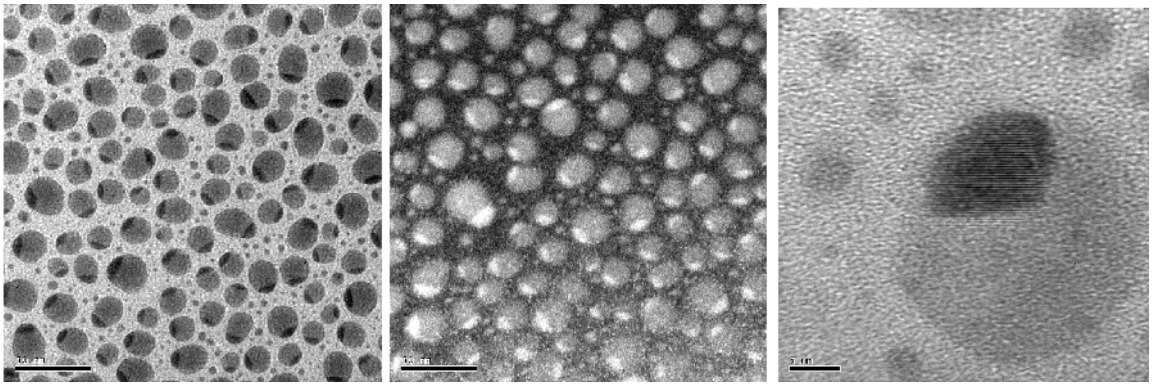

Figure 2: Left:bright field TEM image of a Ga-Pb sample at T=202°C. Center: dark field TEM image

of the same sample at the same temperature. Right: high-resolution TEM image of a particle of the same sample at T=-160°C: we can easily distinguish the monocrystalline structure of the solid Pb-rich phase, as well as its faceted shape.

Figure 2 on the left, displays the general appearance of the Ga-Pb nanosystem as observed by TEM in bright field mode in the case of a sample $Ga_{0.85}Pb_{0.15}$ corresponding to the successive deposition of Ga and Pb layers of respective equivalent thicknesses 3.2 and 0.8nm. We can easily distinguish the uniform contrast of Ga nanodrops and the diffraction contrast of Pb nanocrystals. The Ga nanodrops size distribution is bimodal [5], with a first mode characterized by a Gaussian distribution of droplet sizes and a second one given by a fast decaying tail of the smallest drops. In the main mode, whose Ga size is about 20 nm, it is easy to observe the presence of Pb crystals of about 8nm in size in contact with the Ga/SiO_x inner surface. As the solid Pb crystal diffracts electrons, it appears as a bright structure in dark field electron microscope image (central part) at the same magnification and same temperature. In the right part of Fig.2 a high-resolution TEM is shown for a particle of the same sample at low temperature. The presence of a regular monocrystalline structure in the solid Pb-rich core is clearly visible together with the faceted shape of the core. High resolution observations demonstrate also that no isolated Pb crystal is visible outside the Ga droplets.

3. Results

We focuss now on the results obtained for the sample with 15 at % Pb. In Fig. 3, 12 TEM images of this sample are shown for temperatures ranging from -160 to 346°C. Each picture concerns the same region of the sample but not exactly the same place, due to unavoidable drifts occuring during the increase of temperature..

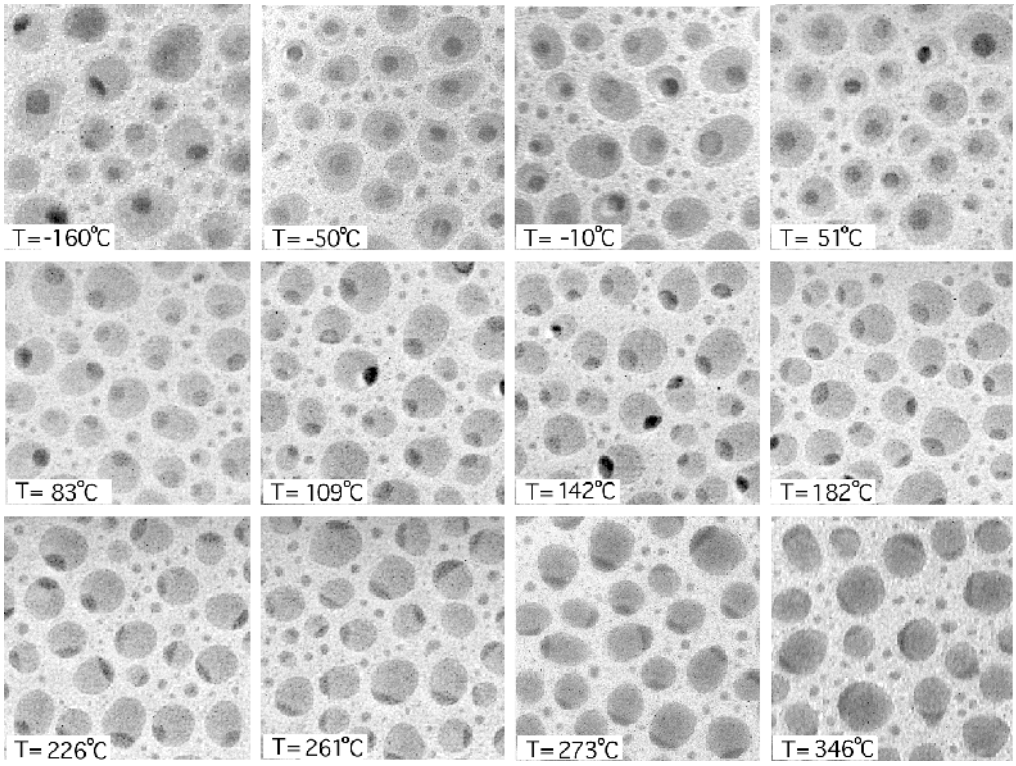

Figure 3: Bright-field TEM pictures illustrating the structure evolution of the $Ga_{0.85}Pb_{0.15}$ sample with temperature. Each picture is a square of 120x120nm^2.

Analysis of shapes and contrasts of the Pb particles, associated to a dark-field observation when necessary, allow to draw conclusions on the different phases of the system.

Ga beeing cooled from room temperature, at T=-160°C it can stay in a deep undercooled liquid state [6]. One can note that two Ga particles (in the upper part of the picture) have solidified. For higher temperatures Ga is in its liquid state.

For temperature below 51°C, Pb is still solid inside liquid Ga. We observe that Pb crystals have a cuboctaedron shape and are mainly located in the center of the Ga nanodrop. This suggests that Pb is mainly in contact with Ga and that there is not an extended Pb/SiOx interface. Futhermore, in some cases, we observe a diffusive movement of the Pb crystal inside the nanodrop.

Above 83°C the situation is qualitatively changing since Pb crystals are now stuck at the Ga/SiOx interface. We therefore clearly have a transition from a dry to wet state of Pb on SiOx. We nevertheless cannot conclude on the continuous or discontinuous nature of this transition. It is important to note that the Pb is still in a solid phase with rounded facets at the Pb/Ga interface. We do not know if we have a Liquid Pb/ SiOx or Solid Pb/SiOx interface but we think that the onset of surface melting is at the origin of this transition to a wet state. As the temperature is increased the contact angle at the triple line between the Pb, Ga and SiOx is clearly decreasing ; this will be described in the next section.

Depending on their sizes, the melting temperature of Pb crystals is situated between 226 and 261°C. This result has been confirmed by high-sensitive optical measurements [2]. We will see in the next section that this melting has not a great influence on the wetting transition scenario, suggesting once again that the solid transition is broadened by surface melting and that we certainly have a Liquid Pb/SiOx interface rather than a Solid Pb/SiOx one.

As the temperature is increased the mixing between Pb and Ga becomes more an more important. Finally an homogeneus liquid state is reached at 443°C for all the particles. It is important to note that the transition is reversible while this is not the case fot solid-liquid Pb or Ga transitions for which a large hysteresis exist.

In the table 1 we summarize the characteristic temperatures of the phase transitions described just above and precise the quantitative differences with the bulk phase diagram. For all transition we roughly have in between 15 and 20 % of relative variation. Note that Ga nanoparticles cristallize in a different phase (e.g. δ phase [6]) than the bulk α phase; this explains the high value found for the relative variation of the melting temperature.

Transition	$\mathbf{T_c}$	$\mathbf{T_{bulk}}$	$\mathbf{(T_{bulk}-T_c)/T_{bulk}}$
Melting of Ga	-34°C	29.7°C	0.21
Melting of Pb	From 226 to 261°	327.5°C	0.16
Miscibility Pb and Ga	443°C	570°C	0.15

Table 1: Characteristic temperatures observed in the $Ga_{0.85}Pb_{0.15}$ sample together with values of the bulk phase diagram and the associated relative variation.

The contact angle θ at the triple line between the three phases (see inset in upper part of Fig. 4) can be measured to characterize the changes in wetting conditions versus temperature. An image analysis of bright-field TEM pictures of the sample has been done for 10 different temperatures in between 50.6 and 346°C. For each temperature, at least 100 particles have been considered and their sizes range roughly in betwenn 10 and 30 nm. Coordinates of the characteristic points of the Ga-Pb meniscus have been recorded and analysed through a Fortran software that perrmits to extract the value of the contact angle θ. In Fig. 4 we plot the size average contact angle as a function of the temperature. It is clear from this figure that θ is a decreasing function of T, i. e that Pb is more an more wetting SiOx as the temperature is increased. Futhermore the system is undergoing a « fully continuous wetting transition » from a dry state to a completly wetting liquid Pb. In the lower part of Fig. 4 we show four pictures illustrationg the transition described juste above. In the region of the Pb melting (200<T<250°C), we do not observe a large variation of the contact angle. This can be due to the size average value of the observed quantity and a more precise investigation is under progress.

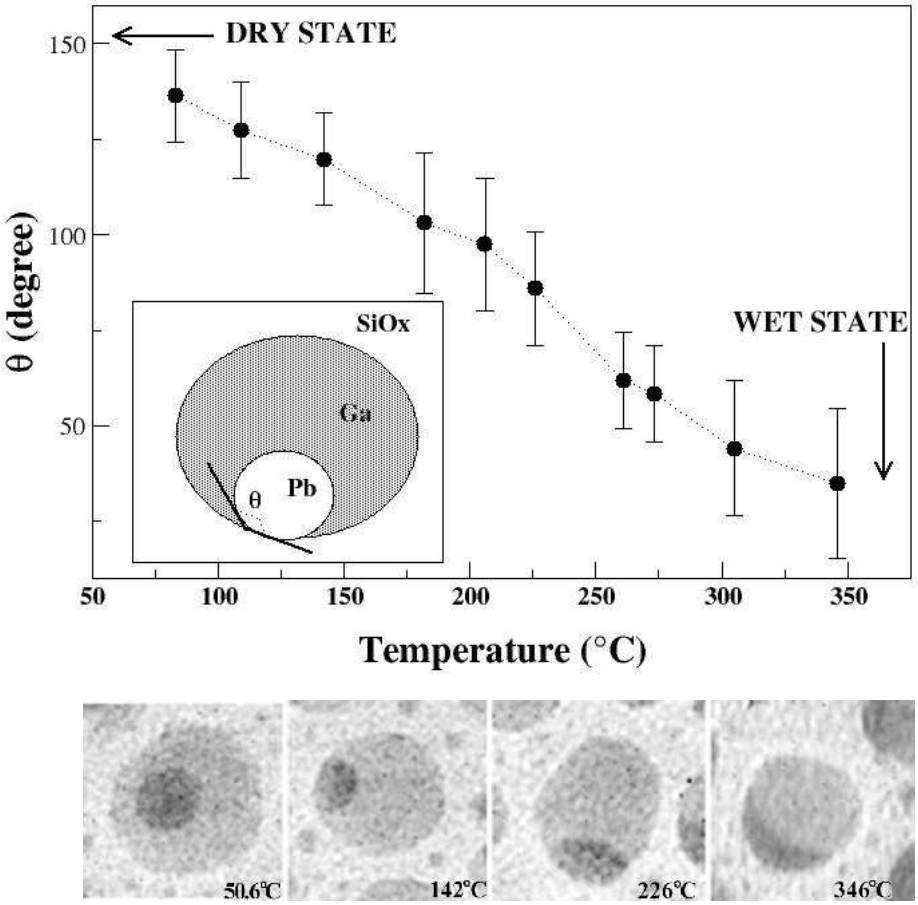

Figure 4: Temperature variation of the contact angle θ (as sketched in inset) at the triple line between the Pb, Ga and SiOx phases. The pictures illustrate the shape evolution of the Pb phase when the temperature is increased (each picture is a square of 30 x30nm^2).

4. Conclusion

In this paper, we have demonstrated that nanoscale Ga-Pb alloys exhibit a phase diagram which is strongly different from the corresponding bulk one. The different values of the melting of Ga, the melting of Pb and the miscibility temperatures are found to be lower than the bulk ones. In all cases the relative variation is in between 15 and 21%.
An image analysis has been done to characterize the transition from the coexistence of Ga and Pb liquids to an homogeneous one. At low temperature the Pb is in contact with Ga but not with SiOx (this is what we call a dry state). At 83°C the Pb starts to wet SiOx, this onset of wetting could be due to the onset of surface melting of the Pb crystal. As the temperature is increased the contact angle is decreasing and the system finally reaches the homogeneous state. The state with a small but non zero value of θ corresponds to a full wetting of Pb on SiOx. In that sense the presented results can be interpreted as a "fully continuous wetting transition" from a dry to a completely wet state. Previous work on larger Ga-Pb binary systems [7] has shown that Ga was completely wetted by Pb, a qualitatively different result than the one presented here. A work is currently in progress to understand the differences observed.

* Corresponding author, present adress : Italian Institute of Technology, via Morego 30, 16163 Genova, Italy

References:

[1] - J.J.Thomson in "Applications of Dynamics to Physics and Chemistry", MacMillan, London (1888)
[2] - R. Kofman, F. Celestini, M. Allione and Y. Lereah in "Highlights on spectroscopies of semiconductors and nanostructures", G.Guizzetti, L.C.Andreani, F.Marabelli, M.Patrini (Eds.), Societa Italiana di Fisica, Bologna, **94** (2007) 421
[3] - I. Ansara and F. Ajersch, J. Phase Equilibria **12**, 73 (1991)
[4] - R. Kofman, M. Allione, F. Celestini, Z. Barkay and Y. Lereah, to appear in EPJD
[5] - E. Søndergard, R. Kofman, P. Cheyssac and A. Stella, Surface Science **364**, 467 (1996)
[6] - A. Defrain, J. Chim. Phys. **74**, 851 (1977)
[7] - D. Chatain and P. Wynblatt, Surface Sci. **345**, 85 (1996)